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HEATS OF FORMATION OF GASEOUS METALLIC HALIDES.(U)  
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# SPACE SCIENCES, INC.

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## INTERIM SCIENTIFIC REPORT

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Attention: Dr. Joseph F. Masi

June 1977



HEATS OF FORMATION OF GASEOUS METALLIC HALIDES

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## I. INTRODUCTION

Reliable data for the gas phase reactions of the diatomic metal compounds are required to assess accurately the candidate species which are potentially significant to chemical laser technology for use by the Air Force in weaponry and defense systems. For example, the dissociation energies for a number of these diatomic oxides and halides are presently undetermined or uncertain. Thus the purpose of the studies conducted under this contract is to obtain experimental data with a high degree of accuracy for certain alkaline earth species important to chemical laser technology.

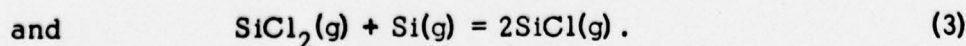
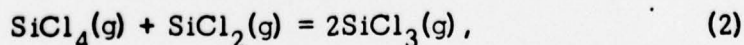
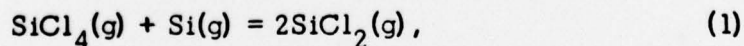
Thus far dissociation energies have been obtained for the diatomic alkaline earth oxides,  $\text{BaO(g)}$ ,  $\text{MgO(g)}$ ,  $\text{SrO(g)}$  and  $\text{CaO(g)}$ , for the alkaline earth monatomic halide  $\text{MgCl(g)}$ , and for  $\text{SiF(g)}$  and  $\text{SiCl(g)}$ . The heats of formation of  $\text{SiF}_2\text{(g)}$ ,  $\text{SiF}_3\text{(g)}$ ,  $\text{SiCl}_2\text{(g)}$  and  $\text{SiCl}_3\text{(g)}$  have also been obtained. Scientific papers involving these eleven species have already appeared or have been submitted for publication in the open literature. The results obtained under the past twelve months effort are described below and a comparison with previously published data is presented.

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## II. RESULTS

### A. Silicon Chlorides

The reaction of  $\text{SiCl}_4\text{(g)}$  with  $\text{Si(c)}$  was studied in the temperature range 1593 to 1792°K. Second and third law reaction enthalpies were determined for



The third law heats of reaction,  $\Delta H_{r298}$ , obtained were  $-30.4 \pm 0.6$ ,  $12.3 \pm 0.5$  and  $27.1 \pm 0.5$  kcal/mole for reactions (1), (2) and (3), respectively.

The heats of reaction yielded third law  $\Delta H_{f298}$  values of  $47.1 \pm 0.6$ ,  $-40.6 \pm 0.6$  and  $-93.3 \pm 0.5$  kcal/mole for  $\text{SiCl(g)}$ ,  $\text{SiCl}_2(\text{g})$  and  $\text{SiCl}_3(\text{g})$ , respectively. A third law dissociation energy value of  $88.6 \pm 0.6$  kcal/mole was calculated for the dissociation of  $\text{SiCl(g)} \rightarrow ({}^3\text{P}_0)\text{Si(g)} + ({}^2\text{P}_{3/2})\text{Cl(g)}$ . The second law  $\Delta H_{f298}$  values from least squares plots of the intensity data (Fig. 1) were  $\text{SiCl(g)} = 45.1 \pm 4$  kcal/mole,  $\text{SiCl}_2(\text{g}) = -40.5 \pm 2$  kcal/mole and  $\text{SiCl}_3(\text{g}) = -95.6 \pm 5$  kcal/mole.

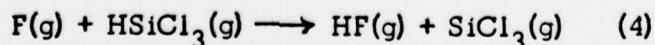
#### 1. Heat of Formation of $\text{SiCl}_2(\text{g})$

The  $\Delta H_{f298}$  value of  $-40.6$  kcal/mole for  $\text{SiCl}_2(\text{g})$  obtained in this study compares favorably with the results of transpiration experiments of Schafer, et al,<sup>1,2</sup> ( $-38.2$  kcal/mole), and of Teichmann and Wolf<sup>3</sup> ( $-38.3 \pm 2$  kcal/mole). Other transpiration and static studies by Chechentsev, et al,<sup>4</sup> Antipin and Sergeev,<sup>5</sup> and Ishino, et al,<sup>6</sup> yielded values for the  $\Delta H_{f298}$  of  $\text{SiCl}_2(\text{g})$  of  $-41$ ,  $-41.5$  and  $-42.5$  kcal/mole, respectively. The JANAF Tables<sup>7</sup> recommend a value of  $-40 \pm 1$  kcal/mole from a review of these experimental results.

#### 2. Heat of Formation of $\text{SiCl}_3(\text{g})$

Analyzing the electron impact studies of Steele, et al,<sup>8</sup> who derived an average value for  $\text{D}(\text{Cl}_3\text{Si-H})$  of  $93 \pm 4$  kcal/mole, the JANAF Tables<sup>7</sup> employed  $-122.6$  kcal/mole for  $\Delta H_{f298}(\text{Cl}_3\text{SiH(g)})$  and calculated  $\Delta H_f \text{SiCl}_3 = -82$  kcal/mole, with an estimated uncertainty of approximately 10 kcal/mole. However, the JANAF Tables adopted  $-96 \pm 10$  kcal/mole for the  $\Delta H_{f298}$  of  $\text{SiCl}_3(\text{g})$  from comparisons with bond energies in the carbon halides and with linear plots of  $\Delta H_f(\text{SiCl}_n)$  versus  $\Delta H_f$  for  $\text{SiF}_n$ ,  $\text{CCl}_n$  and  $\text{CF}_n$ .

Cadman, et al,<sup>9</sup> from an examination of the infrared emission studies of Jonathan, et al,<sup>10</sup> for the reaction



set limits to the  $\Delta H$  of the reaction between  $-40.4$  and  $-50.0$  kcal and



chose -45.2 kcal, since they felt that the upper limit was the better estimate, and thus reported a value of -87.5 kcal/mole for the  $\Delta H_{f298}$  of  $\text{SiCl}_3(\text{g})$ .

Additional non-equilibrium studies have been performed, including an electron impact study by Steele, et al,<sup>8</sup> who calculated a value of  $-69 \pm 4$  kcal/mole for the  $\Delta H_{f298}$  of  $\text{SiCl}_3(\text{g})$  from ionization potentials and ion heat of formation. Wang, et al,<sup>11</sup> performed dissociative electron attachment experiments on  $\text{SiCl}_4(\text{g})$  and assumed the formation of  $\text{Cl}^-$  and  $\text{SiCl}_3(\text{g})$ . Measuring an appearance potential for the  $\text{Cl}^-$  ion of  $1.2 \pm 0.2$  eV and applying a correction of 7.6 kcal/mole for the excess vibrational and transitional energies they calculated a value of  $-81 \pm 5$  kcal/mole for  $\Delta H_{f298}$  of  $\text{SiCl}_3(\text{g})$ . More recently, Pabst, et al, as reported by Franklin<sup>12</sup> from the same laboratory also employed dissociative electron processes and obtained -90 kcal/mole for the  $\Delta H_{f298}$  of  $\text{SiCl}_3(\text{g})$ .

Generally, the electron collisional processes would be uncertain to at least  $\pm 10$  kcal/mole due to a lack of the positive identification of the ionic and radical species and the difficulty in precisely determining the excess energies involved in the process. Likewise, the kinetic processes involving silanes in reactions similar to equation (4) would have similar error limits. A discrepancy of at least 12 kcal/mole is seen from the values of -110 and -122.6 for the  $\Delta H_{f298}$  for  $\text{HSiCl}_3$  reported by Steele, et al,<sup>8</sup> and the latest JANAF Table for this species (December 31, 1969), respectively.

### 3. Dissociation Energy of SiCl

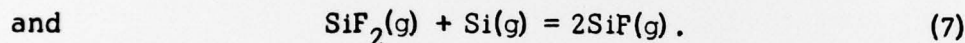
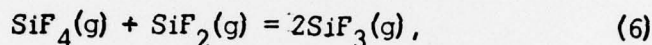
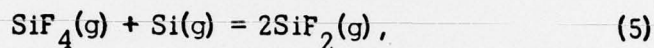
The dissociation energy for  $\text{SiCl}(\text{g})$ ,  $88.6 \pm 0.6$  kcal/mole (or  $88.6 \pm 2$  kcal/mole, including error limits), obtained in these studies lies between those calculated from spectroscopic constants. The spectroscopic constants of Verma<sup>13</sup> were examined by the JANAF Tables scientists,<sup>7</sup> Gaydon,<sup>14</sup> and Kuzyakov,<sup>15</sup> with recommended values of  $90 \pm 15$ ,  $76 \pm 12$ , and  $103 \pm 15$  kcal/mole, respectively, for the dissociation energy of  $\text{SiCl}(\text{g})$ .

### B. Silicon Fluorides

The reaction of  $\text{SiF}_4(\text{g})$  with  $\text{Si}(\text{c})$  was studied in the

temperature range 1590 - 1782°K. A double boiler Knudsen cell arrangement was used in which a stainless steel bulb containing SiF<sub>4</sub> was connected through an alumina tube with a 1 mm diameter annulus to an alumina effusion cell containing metallic silicon. The SiF<sub>4</sub> flow rate was controlled by a variable leak.

Second and third law reaction enthalpies were obtained for



The third law heats of reaction,  $\Delta H_{f298}$ , determined were  $-2.9 \pm 0.25$ ,  $7.8 \pm 0.5$  and  $21.1 \pm 0.5$  kcal/mole for reactions (5), (6) and (7), respectively. The heats of reaction yielded third law  $\Delta H_{f298}$  values of  $-5.8 \pm 0.5$ ,  $-140.6 \pm 0.3$  and  $-259.3 \pm 0.5$  kcal/mole for SiF(g), SiF<sub>2</sub>(g) and SiF<sub>3</sub>(g), respectively. A third law dissociation energy value of  $131.2 \pm 0.5$  kcal/mole was calculated for the dissociation of  $\text{SiF}(\text{g}) \rightarrow ({}^3\text{P}_0)\text{Si}(\text{g}) + ({}^2\text{P}_{3/2})\text{F}(\text{g})$ . The second law  $\Delta H_{f298}$  values obtained from intensity data (Fig. 2) were SiF(g) =  $-3.8 \pm 5$  kcal/mole, SiF<sub>2</sub>(g) =  $-140.3 \pm 2$  kcal/mole, and SiF<sub>3</sub>(g) =  $-259.5 \pm 5$  kcal/mole.

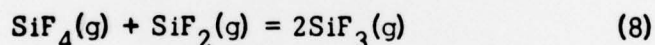
#### 1. Heat of Formation of SiF<sub>2</sub>(g)

The reaction of SiF<sub>4</sub> with Si(c) was studied in a flow system in the temperature range 1400 - 1600°K by Margrave, Kanaan and Pease.<sup>16</sup> The product was assumed to be SiF<sub>2</sub> or its polymer. A heat of formation of  $-148 \pm 4$  kcal/mole for the  $\Delta H_{f298}$  of SiF<sub>2</sub>(g) was reported. Our studies showed that other silicon species account for approximately 30% of the total. From transpiration studies, Schafer, et al,<sup>1</sup> reported  $-139.0$  kcal/mole for the  $\Delta H_{f298}$  of SiF<sub>2</sub>(g). Effusion-mass spectrometer experiments by Ehlert and Margrave<sup>17</sup> involving the reaction of CaF<sub>2</sub> with silicon resulted in  $-140.5 \pm 3$  kcal/mole for the  $\Delta H_{f298}$  of SiF<sub>2</sub>(g),

in excellent agreement with the value of  $-140.6 \pm 0.3$  kcal/mole obtained in our studies.

## 2. Heat of Formation of $\text{SiF}_3(\text{g})$

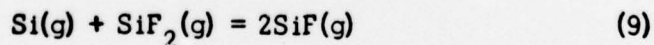
This is apparently the first thermochemical value for the  $\Delta H_f$  of  $\text{SiF}_3(\text{g})$ . Two electron impact studies have yielded  $-235 \pm 20$  kcal/mole for the  $\Delta H_{f298}$ .<sup>18,19</sup> Wang, et al,<sup>19</sup> reported this value from dissociative electron attachment processes to  $\text{SiF}_4$ , while McDonald, et al,<sup>18</sup> determined their value from electron impact studies on  $\text{SiF}_4$  producing  $\text{SiF}_3^+$ . In analyzing the work of McDonald, et al,<sup>17</sup> and that of Wang, Margrave and Franklin<sup>19</sup> the JANAF Supplement dated June 30, 1976 cites a paper by Franklin<sup>20</sup> in which he suggests that the assumption of the fraction of active vibrations as a constant in the previous electron impact studies may have caused a bias of 15 kcal/mole or more in the heat of formation. The JANAF Tables<sup>7</sup> report an estimated value of  $-263 \pm 5$  kcal/mole assuming the  $\Delta H$  of the reaction



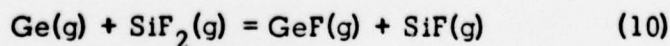
to be 0.5 kcal.

## 3. Dissociation Energy of $\text{SiF}$

Ehlert and Margrave<sup>17</sup> in their effusion-mass spectrometer study also obtained ion intensity data for  $\text{SiF}^+$ . With these data for the reaction



they reported  $129.5 \pm 3$  kcal/mole for the  $D_o$  of  $\text{SiF}$ , which is in good agreement with the present value. Hastie and Margrave<sup>21</sup> from the reaction enthalpy of



obtained  $135 \pm 3$  kcal/mole for the  $D_o$  of  $\text{SiF}$ .

Johns and Barrow<sup>22</sup> reported a value of  $125 \pm 10$  kcal/mole



for the  $D_0$  of SiF from a Birge-Sponer extrapolation of several spectroscopic states. Gaydon,<sup>14</sup> on the other hand, obtained  $115 \pm 12$  kcal/mole for the  $D_0$  from a Birge-Sponer extrapolation of the ground state. Kuzyakov<sup>15</sup> recommended 110 kcal/mole for the  $D_0$  based on a review of the spectroscopic data.

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6. Milton Farber and R. D. Srivastava, "Mass Spectrometric Determination of the Heats of Formation of the Silicon Fluorides  $\text{SiF(g)}$ ,  $\text{SiF}_2\text{(g)}$  and  $\text{SiF}_3\text{(g)}$ ," submitted for publication in J. Chem. Soc., Faraday Transactions I.



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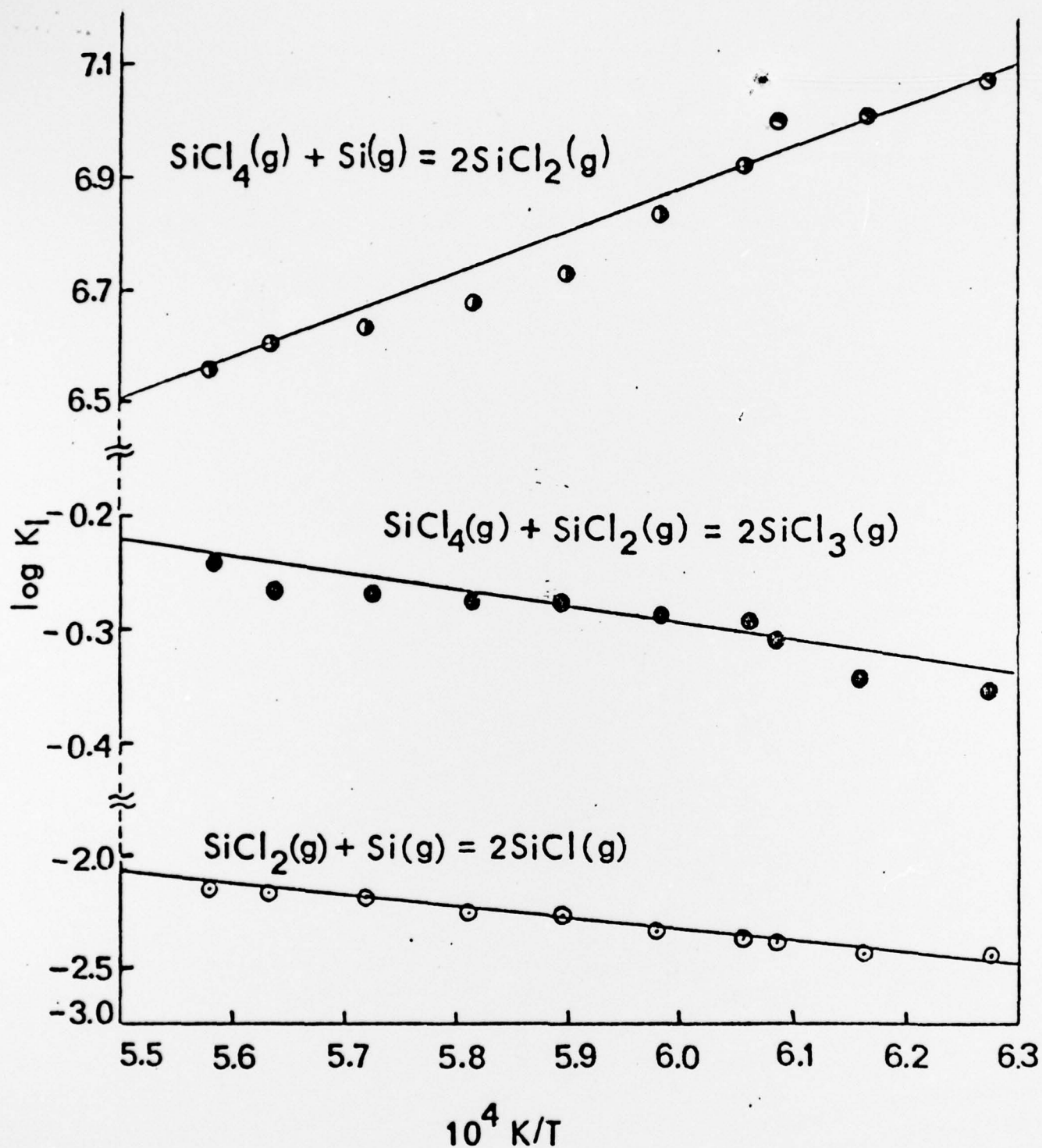


Fig. 1. Plots of the  $\log K_I$  vs.  $1/T$  for the Equilibria involved in the Reactions of  $\text{Si}(\text{c})$  with  $\text{SiCl}_4(\text{g})$

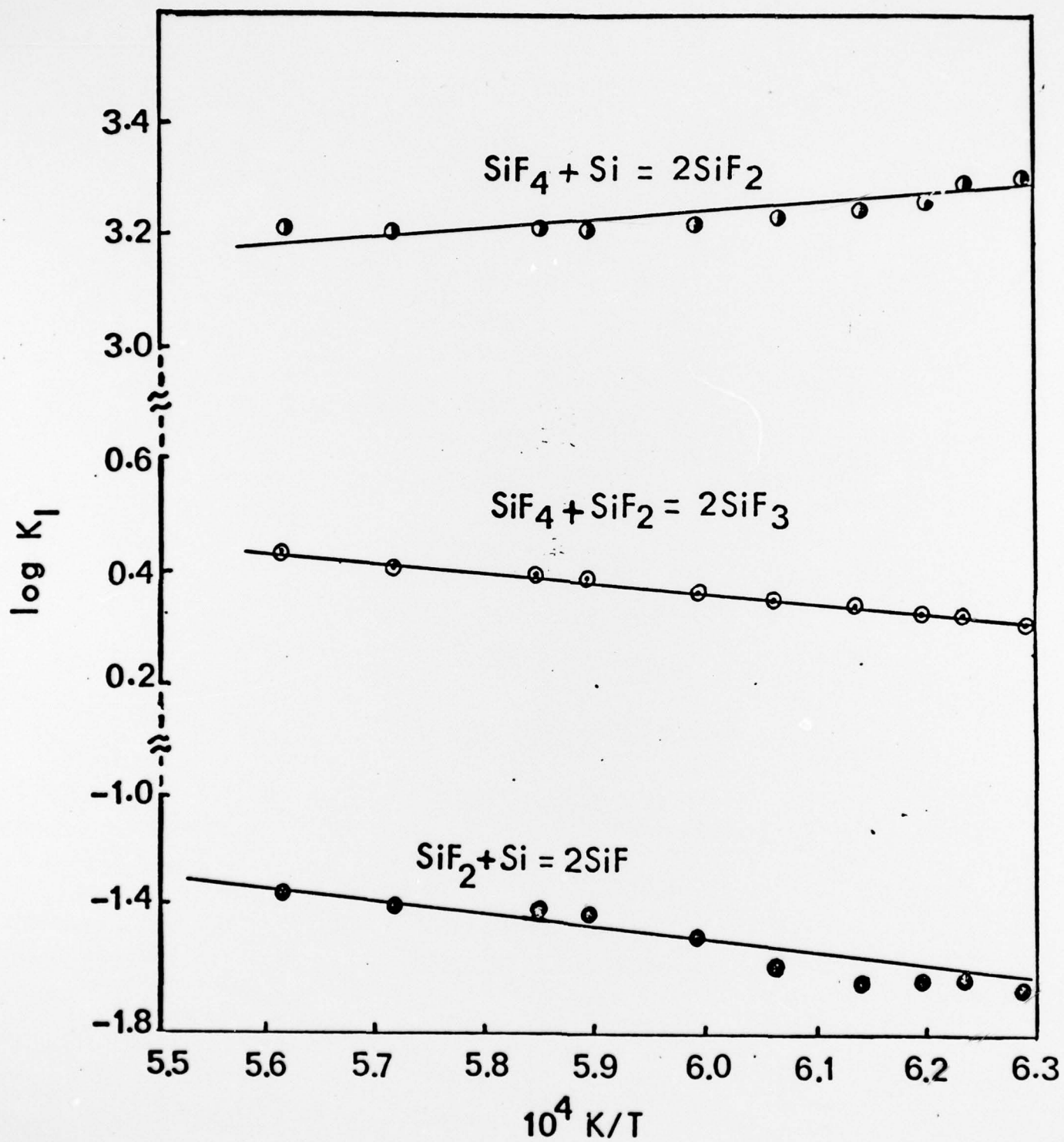


Fig. 2. Plots of the  $\log K_I$  vs.  $1/T$  for the gaseous isomolecular equilibria resulting from the reactions of  $\text{Si(c)}$  with  $\text{SiF}_4(\text{g})$



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The heats of formation and dissociation energies for the silicon subchlorides and silicon subfluorides $\text{SiCl}_3(\text{g})$ , $\text{SiCl}_2(\text{g})$ , $\text{SiCl}(\text{g})$ , $\text{SiF}_3(\text{g})$ , $\text{SiF}_2(\text{g})$ and $\text{SiF}$ were determined from high temperature thermochemical reactions of $\text{SiCl}_4(\text{g})$ and $\text{SiF}_4(\text{g})$ . Ion intensities for the species involved in the reactions were obtained mass spectrometrically, leading to equilibrium constants and reaction enthalpies. The heats of formation were obtained by both second and third law methods and found to be in good agreement. ←			

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